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# DendriMacs and HyperMacs. Emerging as more than just model branched polymers.

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The past decade has seen an emerging interest in the design and synthesis of ever more complex, hierarchically branched polymers – often described as dendritically branched polymers. In part, this has been driven by the long-established desire of both the polymer academic and industrial  
10 (production and process) communities to gain a true understanding of the effects of molecular architecture variables upon polymer properties and the implications for polymer process engineering. However, the intrinsically unique properties associated with such branched polymer systems offers the potential to move beyond ‘model’ polymers. In this paper we will describe some of the most notable work being carried out in this field as well as focussing on work carried out in  
15 our group on the synthesis of DendriMacs and HyperMacs – a methodology which is emerging as one the most effective and versatile of the synthetic methodologies reported to date.

## 1. Introduction

It has long been understood that the physical properties of polymeric materials depend to a very large extent on the  
20 molecular architecture of the constituent polymer chains. Variables such as molecular weight, polydispersity and the presence and degree of branching in polymers have huge implications not only for the final solid state properties of a product but also for properties in the melt. Of course, these  
25 parameters strongly impact upon rheology and processing. To understand the relationship between the molecular architecture and the physical properties of polymers; to quantify the effects and even to go further and be able to predict how the molecular structure could be altered to modify  
30 physical properties is a laudable and realistic ambition. However, to attain that goal using industrial materials, which often have a very broad distribution of structures, would be an exercise in futility. It is this realisation that has driven synthetic polymer chemists in recent decades to design model  
35 branched materials which are structurally homogeneous i.e. polymers with a narrow molecular weight distribution and in the case of branched polymers, with a well-controlled branching distribution. The synthesis of well-defined molecular architectures such as star branched polymers<sup>1,2</sup>,  
40 mikto star polymers<sup>3-5</sup> and H-shaped polymers<sup>6,7</sup> have contributed much over the years to the understanding and prediction of the relationship between structure and properties. However, more recently, strategies have been devised to synthesise yet more complex, hierarchically,  
45 branched architectures with a variety of resulting structures and differing degrees of control over molecular structure. The variety of synthetic methodologies tend to result in polymers which can be divided into two categories. The first category might be described as long-chain branched analogues of  
50 dendrimers and has been given a plethora of different names

including, dendrimer-like (star) polymers<sup>8</sup>, Cayley Trees<sup>9</sup>, dendritic polymers<sup>10</sup> and DendriMacs<sup>11</sup> (see figure 1) but what unites them is that they are all prepared by a series of iterative reactions and the resulting polymers have a dendrimer-like  
55 structure in which there is a well-defined linear polymer chain between branch points. As is the case with classical dendrimers, their long-chain branched cousins may be prepared by either a convergent<sup>12</sup> or divergent<sup>13,14</sup> approach and the relative merits of these approaches will be discussed  
60 in detail.

The second category might similarly be described as the long-chain branched analogue of hyperbranched polymers in so much that the synthesis results in materials that are often polydisperse in both molecular weight and architecture. Once  
65 again this category comprises of many variations of branched structure with differing degrees of structural homogeneity. Terms such as dendrigraft<sup>15-18</sup>, Comb-burst<sup>19</sup>, arborescent<sup>20</sup>, hyperbranched<sup>21</sup> and HyperMacs<sup>22</sup> have all been used to describe branched polymers of this type.

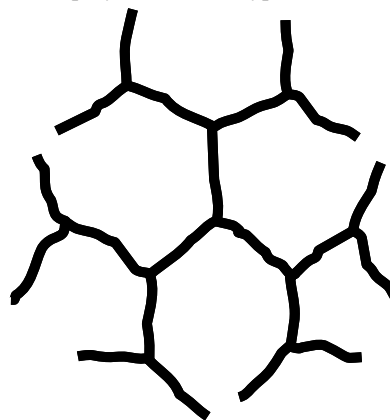


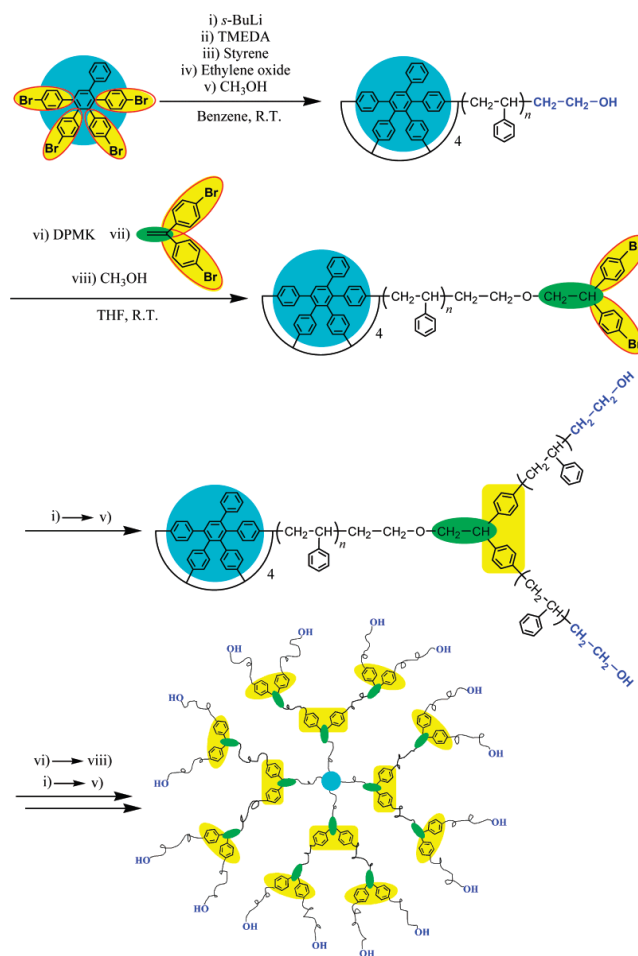
Figure 1. Schematic of dendritically branched polymer

The synthesis of both categories of hierarchically branched polymers, almost without exception involves a combination of living or controlled polymerisation such as anionic, cationic or atom transfer radical polymerisation with branching reactions or coupling reactions. In this paper we will discuss the merits and limitations of the the major contributions to this field and focus on our contribution – namely DendriMacs and HyperMacs. Although similarities may be drawn between our work and others in so much that the type of branched structures attainable have much in common we believe that the use of macromonomers in the synthesis of DendriMacs and HyperMacs is emerging as one of, if not the most versatile and effective methodologies to make branched polymers that fall into both categories.

## 2. Well-Defined Dendritically Branched Polymers

Various strategies have been developed to prepare dendritically branched architectures of the type shown in Figure 1, with the principal aim being to control all of the molecular parameters of the final structure in order to minimise structural heterogeneities. Notable contributors to this field include Hadjichristidis<sup>10,23</sup>, Gnanou<sup>24-26</sup>, Hedrick<sup>8</sup>, Hirao<sup>27-30</sup> and Monteiro<sup>31-33</sup>. It should be noted that the synthesis of such materials always follows an iterative, multi-step methodology, is time consuming and often results in the production of relatively modest quantities of material. Furthermore, just as there are two general strategies for the synthesis of dendrimers, there are similarly two general approaches for preparing dendritically branched polymers; a divergent and convergent approach. The earliest examples<sup>13,14</sup> of dendrimer synthesis were carried out via a *divergent* approach in which the molecule is built from the core out towards the periphery. As the number of generations increases there is a rapid increase in the number reactive sites at the chain ends and with each reaction step potential problems increase. Firstly, any incomplete reaction of these terminal groups leads to imperfections in the subsequent generation and the probability of these imperfections occurring increases as the growing molecule increases in generations. Furthermore as the number of reactive groups increase it can become progressively more difficult to detect any possible imperfections, especially in the case of the macromolecular dendritically branched polymer of the type described here, where the concentration of chain ends is very low with respect to the molecular mass. An alternative *convergent* approach for dendrimer synthesis was first reported by Hawker and Fréchet in 1990<sup>12</sup>. This approach offers distinct advantages in that the molecule is built from what will ultimately become the periphery and, at each step, growth is designed to occur via a very limited number of reaction steps. Furthermore, in the case of long chain branched analogues of dendrimers, each coupling reaction can be analysed by size exclusion chromatography. Incomplete reaction results in partially coupled material which is easily detected and in some cases, imperfectly branched material can be removed by fractionation.

### 2.1 Divergent Strategies Gnanou has reported the synthesis



**Scheme 1** Divergent synthetic strategy to third generation dendrimer-like polystyrene developed by Gnanou<sup>24</sup> (Copyright © ACS)

of dendrimer-like polystyrene by atom transfer radical polymerization (ATRP) via a divergent methodology<sup>25</sup>. Using multifunctional calixarene-based initiators for ATRP of styrene and end group modification reactions, third generation dendrimer-like structures were obtained. However, the polymerisations had to be stopped at low monomer conversions to prevent irreversible coupling reactions between growing species and the polydispersity values of the resulting structures were not narrow, in the region of 1.25-1.4. More recently Gnanou<sup>24</sup> reported a novel divergent strategy (see scheme 1) for the synthesis of well defined dendrimer-like samples of polystyrene up to the seventh generation and polybutadiene up to the third generation. Asymmetric structures and miktoarm stars were also reported. The reported strategy relies on lithium-halide exchange reactions to generate multicarbanionic species which may be used as multifunctional initiators and on the design of a reagent that can concomitantly react with living carbanionic chains/arms to terminate them and then yield multicarbanionic sites after lithiation of the bromide functionalities with butyllithium. This reagent, 4,4'-dibromodiphenylethylene, functions as a TERminating agent and a Multifunctional INITiator – a so called TERMINI agent. Hedrick also adopted a divergent

approach with the living ring opening polymerization of  $\epsilon$ -caprolactone followed by functionalization and deprotection. The polydispersity of the resulting structures remained relatively narrow with values in the range 1.06-1.16. The divergent approach has been implemented very successfully by Hirao<sup>27-30</sup> to synthesize dendrimer-like PMMA. In this case a series of iterative steps involving a coupling reaction of  $\alpha$ -functionalized living anionic PMMA with benzyl bromide moieties was carried out. Up to seven generations of branching was attained with narrow molecular weight distributions (polydispersities of less than 1.05) although detecting imperfections in the structure would become a near impossibility at higher generations, an inherent problem with all divergent strategies. Furthermore it is likely that this methodology could not produce such well defined structures from other monomers such as styrene or dienes because of less favourable rates of initiation in these cases.

**2.2 Convergent Strategies** Hadjichristidis<sup>10,23</sup> describes the synthesis of well-defined second and third generation dendritic polymers based on stepwise convergent anionic polymerization and chlorosilane coupling reactions, although there is some inconsistency in the nomenclature and what Hadjichristidis describes as second and third generation we (and others) describe as first and second generation. Whilst the resulting polymers are undoubtedly highly branched, the nature of the chemistry, requiring multiple reaction steps to be carried out under high vacuum conditions to maintain an inert atmosphere is very challenging and the generation of imperfections in the structure is inevitable – a fact acknowledged by the authors of that work<sup>23</sup>. The presence of such imperfections must be considered carefully when attempting to relate molecular architecture to rheological properties. More recently Monteiro et al<sup>31-33</sup> have reported the synthesis of dendritically branched polymers prepared using a combination of atom transfer radical polymerisation (ATRP) and click chemistry coupling reactions in a convergent coupling strategy. Linear polymers were prepared via ATRP and the appropriate groups (azide and alkyne) required for the click reaction introduced at the chain ends. This methodology beautifully demonstrates the versatility of a “macromonomer” approach with the authors reporting branched polymers comprising of polystyrene and polyacrylate segments. However, ATRP undoubtedly places certain limitations on the molecular weight and polydispersity of the linear segments and one suspects that it would be challenging to make materials suitable for structure-property correlation studies where optimal control over the molecular structure is required.

### 3. Dendrigraft/Hyperbranched polymers

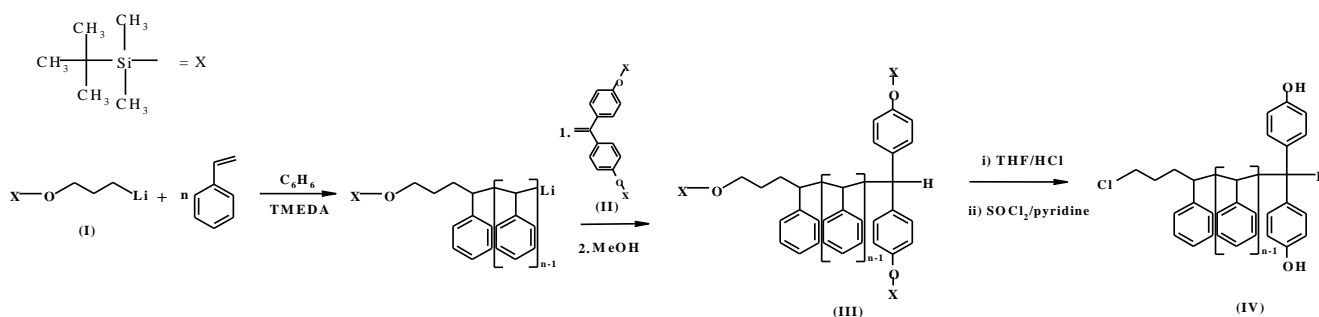
Each of the strategies described above aims (with varying degrees of success) to control all of the molecular parameters of the resulting branched architectures i.e. the molecular weight and polydispersity of the linear polymer segments, the degree of branching and the position of branch points. However, in all cases the necessary multiple reaction steps results in very time consuming syntheses and on occasion



**Scheme 2** Convergent synthetic strategy for the preparation of hyperbranched polyisobutylene, developed by Puskas<sup>35</sup> (Copyright © ACS)

poor yields of material. There other highly branched polymers which are less well defined in terms of their molecular parameters – often polydisperse in terms of molecular weight and/or architecture – but which offer the advantage of simplicity of synthesis and the ability to create useful quantities of material. Dendrigraft polymers<sup>15</sup> have been described as semi-controlled branched polymer architectures in which branch points are randomly distributed but which are still characterised by narrow molecular weight distributions. Dendrigraft polymers are typically obtained by living/controlled polymerisation in combination with grafting/branching reactions. Arborescent polymers – one class of dendrigraft polymers – were first reported by Gauthier and Möller in 1991<sup>20</sup>. Reactive functionalities such as chloromethyl groups were introduced onto the linear polystyrene chains. Living polystyryllithium chains prepared by anionic polymerisation and end-capped with diphenylethylene were then added to the chloromethylated PS and a grafting reaction yields a comb-like structure. Additional chloromethylation and grafting cycles results in the highly branched arborescent polymers. This strategy can also be used to prepare polydiene analogues and branched copolymers<sup>15</sup>. A similar ‘divergent grafting onto’ strategy was used by Tomalia et al<sup>19</sup> to synthesise comb-burst<sup>®</sup> polyethyleneimines. This work involved successive cationic grafting reactions of living poly(2-ethyl-2-oxazoline) chains onto polyethyleneimine substrates. Grubbs<sup>34</sup> et al described the synthesis of dendrigraft polymers via a divergent ‘grafting from’ strategy based on living radical polymerisation. Linear polystyrene containing randomly distributed chloromethyl groups was prepared by nitroxide mediated free radical polymerisation of styrene and *p*-(4'-chloromethylbenzyloxymethyl)styrene. The chloromethyl groups were then reacted with the sodium salt of a hydroxy-terminated TEMPO-styrene adduct and a graft polymer obtained by the copolymerisation of styrene and *p*-(4'-chloromethylbenzyloxymethyl)styrene initiated by the TEMPO functionality. The chloromethyl groups on the grafted chains are then used to initiate the polymerisation of styrene via ATRP to yield the dendrigraft structure.

Two notable contributions to the synthesis of long chain



**Scheme 3** Synthesis of polystyrene AB<sub>2</sub> macromonomer

hyperbranched polymers using convergent strategies have been described. Puskas and co-workers first reported the synthesis of hyperbranched polyisobutylene by a convergent cationic polymerisation which was a modified self-condensing vinyl polymerisation (SCVP). A small amount of inimer, either 4-(2-hydroxyisopropyl)styrene<sup>21</sup> or 4-(2-methoxyisopropyl)styrene<sup>35</sup> was copolymerised with isobutylene whereby the *tertiary* hydroxyl or methoxy functionality on the inimer are effective initiators for the living cationic polymerisation of isobutylene and the vinyl group present at the end of each growing chain allows it to react as a macromonomer. As the reaction proceeds, highly branched polyisobutylene is formed without the loss of propagating sites. Knauss<sup>36-38</sup> reported the synthesis of dendritically branched polystyrene prepared by a convergent method using anionic polymerisation. Styrene was polymerised in the presence of either vinylbenzyl chloride (VBC) or 4-(chlorodimethylsilyl)styrene (CDMSS). Each of the comonomers is capable of a dual role; the vinyl group enables VBC and CDMSS to take part in the polymerisation and the chloromethyl/chlorosilane functionality are susceptible to nucleophilic attack by polystyryllithium resulting in the introduction of a branching point. By controlling the addition rate of the difunctional comonomer/coupling agent and the molar ratio of styrene to comonomer a variety of branched polymers were prepared with molecular weights ( $M_n$ ) up to 600,000 g mol<sup>-1</sup>, polydispersity indices of 1.1-1.4 and average generation numbers up to 5.8. One further notable recent contribution to the group of highly (hyper)branched polymers is the work of Frey who adopted a facile approach to prepare highly branched polydienes<sup>39,40</sup>. Their strategy involves the synthesis of polydienes (both polybutadiene and polyisoprene) by living anionic polymerisation in THF to yield a low 1,4 microstructure and a large number of pendant vinyl groups. The living polymers were endcapped with chlorodimethylsilane to give an AB<sub>n</sub> type macromonomer. These macromonomers were then polymerised in the bulk by a hydrosilylation reaction using Karstedt's catalyst. Although this approach is indeed facile and successfully gave branched polymers the desired intermolecular coupling reactions were somewhat hampered by competing intramolecular cyclisation reactions. This is, of course, a possibility with all AB<sub>n</sub> macromonomers but inevitably becomes more of an issue when the number of B functionalities 'n' is a large number as is the case in Frey's work.

## 4 DendriMacs and HyperMacs

Our contribution to this still growing area of polymer science has been the development of DendriMacs and HyperMacs. DendriMacs and HyperMacs are essentially long chain branched analogues of classical dendrimers and hyperbranched polymers; analogous in terms of both structure and mode of synthesis. Where dendrimers and hyperbranched polymers may be synthesised using low molecular weight AB<sub>2</sub> monomers, DendriMacs and HyperMacs are prepared from  $\alpha,\omega,\omega'$  – trifunctional AB<sub>2</sub> macromonomers. The macromonomers are coupled using a Williamson coupling reaction to afford the branched polymer.

### 4.1 Synthesis of Polystyrene Macromonomers

When considering not only the design but also the synthesis of the macromonomer building blocks, our prime objectives were to quantitatively introduce the relevant chain-end functionalities that would facilitate subsequent Williamson coupling reactions and to retain optimal control over both the molecular weight and the polydispersity. Anionic polymerisation is a living polymerisation technique with no intrinsic termination reaction and produces polymers of well-defined molecular weight and narrow polydispersity. The living nature of the polymerisation also allows for the quantitative introduction of functional groups at either end of the polymer chain by using suitable initiators and terminating agents and as such, anionic polymerisation is the perfect technique for macromonomer synthesis. Using a commercially available lithium initiator, 3-*tert*-butyldimethylsiloxy-1-propyllithium (FMC InitiaLi 103) containing a protected primary alcohol functionality and an readily synthesised diphenylethylene derivative containing two protected phenol groups in a controlled termination reaction, we were able to synthesise polystyrene AB<sub>2</sub> macromonomers. Following deprotection of the alcohol groups by a mild acid hydrolysis and conversion of the primary alcohol to an alkyl halide the macromonomers can be used to build up novel highly branched polymeric architectures – see Scheme 1<sup>22</sup>. Anionic polymerisation offers the possibility to prepare polymers with a range of molecular weights and degree of control simply not possible by any other polymerisation mechanism and a range of macromonomers with molecular weights from a few thousand to nearly 100,000 g mol<sup>-1</sup> have been prepared.



**Table 1.** Molecular weight, polydispersity and intrinsic viscosity data for HyperMacs synthesized from AB<sub>2</sub> macromonomers where 'A' is chlorine, base is potassium carbonate and reaction carried out in DMF at 160 °C

Macromonomer	M <sub>n</sub> /gmol <sup>-1</sup>	Dp <sub>n</sub>	M <sub>w</sub> /gmol <sup>-1</sup>	Dp <sub>w</sub>	PDI	[η] <sub>hyper</sub> /dlg <sup>-1a</sup>	[η] <sub>lin</sub> /dlg <sup>-1b</sup>	g <sup>c</sup>
1 (3,600 gmol <sup>-1</sup> )	16,100	4.5	36,600	9.6	2.2	0.145	0.227	0.63
2 (6,300 gmol <sup>-1</sup> )	33,600	5.3	65,400	10.1	1.9	0.226	0.343	0.65
3 (12,400 gmol <sup>-1</sup> )	52,600	4.2	167,400	13.0	3.2	0.415	0.671	0.62
4 (16,800 gmol <sup>-1</sup> )	88,000	5.2	298,000	17.3	3.4	0.568	1.011	0.56
5 (37,300 gmol <sup>-1</sup> )	185,100	5.0	555,800	14.3	3.0	0.937	1.576	0.59
6 (94,000 gmol <sup>-1</sup> )	565,400	6.0	1,630,000	15.6	2.9	1.808	3.391	0.53

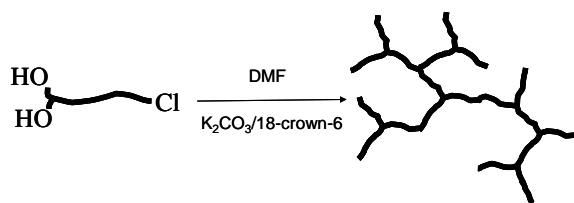
<sup>a</sup> Measured by SEC viscometry.

<sup>b</sup> Calculated using the Mark-Houwink equation [η] = KM<sup>a</sup>.

<sup>c</sup> g<sup>c</sup> = [η]<sub>hyper</sub>/[η]<sub>linear</sub>.

less suitable as 'model' branched polymers but that is not necessarily the case – more of which later!

Polystyrene AB<sub>2</sub> macromonomers, functionalised with two phenolic alcohol functionalities at one chain end and an alkyl chloride group at the other chain end were prepared (Scheme 1) with molecular weights ranging from approximately 4,000 to 94,000 gmol<sup>-1</sup> (Table 1). HyperMacs were prepared by a polycondensation (Williamson) coupling reaction in DMF (Scheme 5) in a similar fashion to that described for polystyrene DendriMacs. It can be seen from the data in Table 1 that the coupling strategy was successful but when the halogen leaving group is chlorine, the coupling reactions had to be carried out in refluxing DMF in order to efficiently generate the branched structures and the extent of the coupling reaction was apparently hampered by side reactions with impurities generated by degrading DMF.

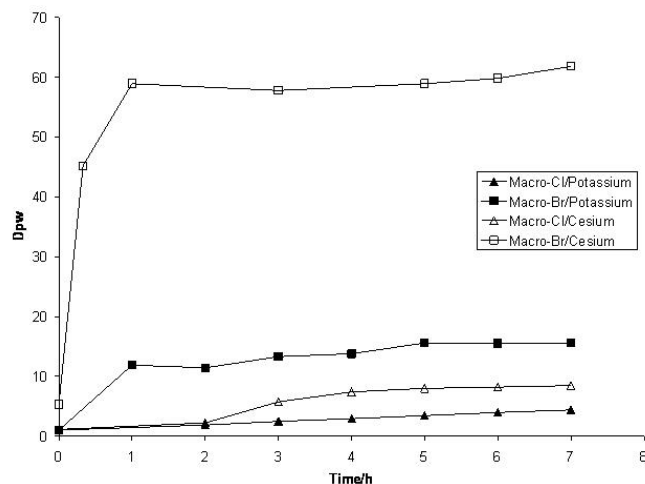


**Scheme 5** Synthesis of polystyrene HyperMac

We find it most convenient to describe the extent of the coupling reaction in terms of the degree of polymerisation, Dp. Hence Dp<sub>n</sub> is M<sub>n</sub>(HyperMac)/M<sub>n</sub>(Macromonomer) and Dp<sub>w</sub> is given by M<sub>w</sub>(HyperMac)/M<sub>w</sub>(Macromonomer). As AB<sub>2</sub> coupling reactions of this type proceed, M<sub>w</sub> and therefore Dp<sub>w</sub> increases more rapidly than M<sub>n</sub> and Dp<sub>n</sub>. It can be seen from the data in Table 1 that these coupling reactions generate HyperMacs with values of Dp<sub>n</sub> of 4.2 – 6.0 and values of Dp<sub>w</sub> of 9.6 – 17.3. Analysis of the HyperMacs by size exclusion chromatography (SEC) showed the presence of a significant amount of uncoupled macromonomer and the presence of dimers, trimers and other species with a low degree coupling. The relationship between molecular weight of macromonomer and extent of coupling reaction is discussed elsewhere<sup>22</sup>. However, despite these modest degrees of coupling the resulting HyperMacs were undoubtedly branched. The branching factor (g<sup>c</sup>) is defined as the ratio of the intrinsic viscosity [η] of a branched polymer to that of a linear polymer of the

same molecular weight. Branched polymers in solution have smaller hydrodynamic volumes, are more compact than linear polymers of identical molecular weight and therefore have relatively lower intrinsic viscosities – hence g<sup>c</sup> for a branched polymer will be less than unity. Values of g<sup>c</sup> were obtained for each HyperMac (see Table 1) and the data lies within a reasonably narrow range (0.53–0.65) confirming that HyperMacs possess a branched structure. Furthermore these data compare very favorably with the data reported by Hirao<sup>29</sup> for well-defined, narrow polydispersity dendrimer-like polymers who reported values for g<sup>c</sup> of 0.80, 0.59 and 0.46 for a first, second and third generation dendrimer-like polymethyl methacrylate.

**Figure 2** The effect of macromonomer leaving group and base on the extent of Williamson coupling reaction (DMF/100 °C) used to prepare HyperMacs from polystyrene AB<sub>2</sub> macromonomer



More recently we have developed the coupling chemistry to significantly enhance the efficiency and extent of the branching reaction<sup>42</sup>. Our objective was to increase the rate of the Williamson coupling reaction to an extent that would allow us to carry out the reactions at much lower temperatures – thereby avoiding any degradation of the DMF. With this aim we considered two possible ways in which the Williamson reaction could be improved – by changing the leaving group and/or changing the base. It can be seen from the data in Figure 2 that changing the leaving group from chlorine to bromine resulted in both an increase in the rate and extent of coupling reaction. At 100 °C the chlorinated macromonomer (using potassium carbonate as

the base) reacts very slowly to a value of  $Dp_w$  of about 4 after 7 hours. The brominated macromonomer of identical molecular weight showed a higher rate and extent of reaction under the same conditions. In Figure 2 it can be seen that the  $Dp_w$  rises up to a value of about 11 during the first hour followed by a more gentle increase up to 15.5 after 7 hours. Data collected after 24 hours (not shown on graph) indicated that the reaction was still proceeding during this period with a final value of  $Dp_w$  of a little over 17. Although replacing chlorine with bromine as the leaving group results in a marked increase in both the rate and extent of reaction the results obtained for the brominated macromonomer are not really an improvement over the original work (table 1) – albeit that the reactions were carried at temperatures which were 60° C lower. In order to further improve the efficiency of these reactions the use of cesium carbonate was investigated. It has been described in the literature that cesium carbonate is a particularly efficient base for Williamson coupling reactions of this type in DMF due to the greater solubility of both cesium carbonate and the resulting phenolate<sup>43</sup>. Although there was some notable improvement in the extent of the coupling reactions when using cesium carbonate instead of potassium carbonate the improvement was again, modest. However, when cesium carbonate was used with the more efficient leaving group – bromine – the improvement in both the rate and extent of the coupling reaction was dramatic. After one hour the  $Dp_w$  had risen to nearly 60 after which there was little increase in  $Dp_w$ . The combined effect of bromine as a leaving group and cesium carbonate as the base far exceeded what we might have expected given the previous results and suggests a synergistic effect of these two modifications. It can be claimed with confidence that this combination overcame the previous solvent related problems!

## 5 Model Polymers?

There can be little doubt about the contribution that well-defined ‘model’ branched polymers have made to the field of understanding polymer properties – in particular melt rheology and the implications that rheology has on polymer processing. It is also apparent from the huge advances in the modelling and prediction of the melt rheology of branched polymers<sup>44-47</sup> that the hierarchical branching of DendriMacs combined with the high degree of structural homogeneity should make them the optimal branched architecture for structure-property correlation studies. However, the challenging and time consuming nature of the chemistry is a major drawback. It should also be said that polystyrene is also not the ideal polymer from which to make DendriMacs. In order to obtain meaningful rheological data from such a polymer it is essential that the molecular weight between branch points be several times the entanglement molecular weight,  $M_e$ . Polystyrene has one of the higher known values of  $M_e$  (c. 16 Kg mol<sup>-1</sup>)<sup>48</sup> and constructing a DendriMac from macromonomers with molecular weights approaching 100,000 gmol<sup>-1</sup> would be extremely challenging. The solution to this challenge is to use a polymer with a lower value of  $M_e$  – polybutadiene – which has a value of  $M_e$  a

little under 2,000 gmol<sup>-1</sup><sup>49</sup>. Fortunately the macromonomer strategy developed in our laboratory to synthesise DendriMacs and HyperMacs is versatile and with only a few minor modifications the synthetic methodology outlined in scheme 4 can be adapted to produce polybutadiene DendriMacs.

### 5.1 Polybutadiene DendriMacs

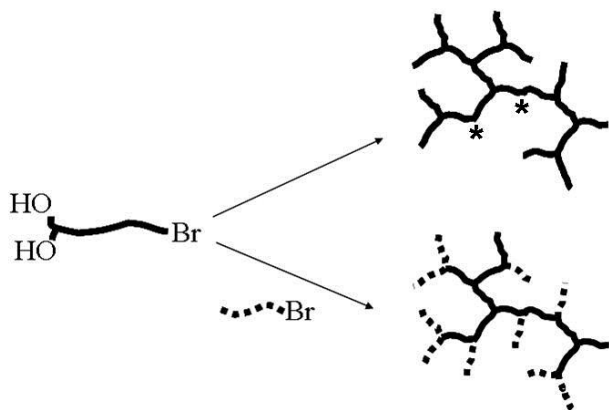
There are two points that need to be addressed in order to transpose the methodology developed to prepare polystyrene DendriMacs (and HyperMacs) to make analogous branched polymers from polybutadiene. Firstly, polybutadiene is insoluble in the ‘textbook’ polar solvents recommended for Williamson coupling reactions (dimethyl formamide, dimethyl acetamide, acetone etc) and secondly with so many reaction steps one has to be aware of the susceptibility of polybutadiene for oxidative degradation. The latter can be ‘managed’ by carrying out reactions under inert atmospheres or under high vacuum conditions and the addition of antioxidant. The former issue required a certain amount of trial and error. In light of the improvements to the coupling reactions discussed above, macromonomers of polybutadiene were prepared by living anionic polymerisation in hexane with an alkyl bromide end group. The optimal solvent for the Williamson coupling reactions proved to be a mixed solvent of tetrahydrofuran and dimethylacetamide (50/50 v/v)<sup>50</sup>. The former being a good solvent for polybutadiene but with a modest dielectric constant whereas the latter is a poor solvent for polybutadiene but has a high dielectric solvent and is therefore a good solvent to promote Williamson coupling reactions. Cesium carbonate was used as the deprotonating base and the coupling reactions were carried out at 60-70 °C for 24 hours. A G1 polybutadiene DendriMac has been successfully prepared<sup>50</sup> and the synthesis of a G2 polybutadiene DendriMac is well underway. Characterisation of the rheological properties of the G1 DendriMac have been undertaken and a comparison made between experimental data and theoretical predictions. The results of these studies will be described in a forthcoming publication.

### 5.2 ‘Model’ Polystyrene HyperMacs

As mentioned previously it might be assumed that the polydisperse nature of HyperMacs would make them unsuitable as ‘model’ branched polymers but that is not the case. Although HyperMacs do not possess the perfectly branched structure of DendriMacs, an intriguing possible application of this methodology is to synthesise ‘model’ analogues for the branched polymers created using metallocene catalysts. The rheology of such polymer melts may be tailored by the controlled addition of long-chain branches using “open-site” metallocene catalysts and the molecular mechanism of vinyl-group reincorporation leads statistically to the same one-parameter topological family of branched structures as the “AB<sub>2</sub>” polycondensation



described here<sup>47</sup>, the only difference lying in the exponential polydispersity of the molecular weight between branches in the case of the metallocene catalysed system. An entangled model system intermediate between the doubly-random ensemble of the metallocene catalysed polymers and the perfectly branched DendriMacs could be a powerful tool in developing predictive approaches to melt rheology. Ideally such “model” HyperMacs would be randomly branched and polydisperse but with a uniform molecular weight between branch points. Whilst the methodology described above (scheme 5) uses macromonomers with well-defined and narrow molecular weight distributions, the coupling reactions yield branched polymers with a distribution of molecular weights between branch points arising from incomplete branching. This incomplete branching results in molecular weights between branch points equal to some multiple of the molecular weight of the macromonomer (see the upper structure in Scheme 6). However, it should be possible to remove this heterogeneity by carrying out coupling reactions of AB<sub>2</sub> macromonomers in the presence of macromonomers functionalised with only an A group. In theory, the addition of up to 50 mol percent of A macromonomer with respect to AB<sub>2</sub> macromonomer should not reduce the overall extent of branching but should ‘mop up’ any unreacted B functionalities (scheme 6) – in practice the use of a slight excess above 50 mol% of A macromonomer w.r.t AB<sub>2</sub> macromonomer should ensure a uniform molecular weight between branch points. This is work in progress.

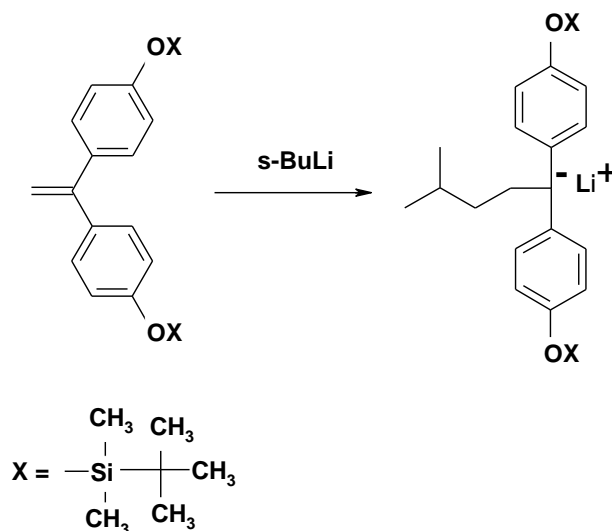


**Scheme 6** A schematic cartoon of the synthesis of HyperMac with uniform molecular weight between branch points – note the incomplete branching (indicated by \*) in the HyperMac formed in the absence of A macromonomer.

## 6. Ongoing and Future Work

The macromonomer approach to synthesise DendriMacs and HyperMacs is only one of a number of strategies adopted to make dendritically branched polymers but this approach is emerging as probably the most versatile methodology and possibly the optimal methodology for generating defect free model polymers with the highest degree of structural homogeneity for structure-property correlations studies. Although some preliminary rheological studies have been

carried out on polystyrene HyperMacs<sup>32,51</sup> the true value of the macromonomer approach to produce model polymers will emerge when investigations into the rheological properties of the polybutadiene DendriMacs is completed.



**Scheme 7.** Bis phenol functionalised diphenylhexyllithium initiator for polymerisation of PMMA macromonomer

Furthermore, ongoing work is beginning to give us some idea of how versatile the macromonomer approach is. As well as synthesising the polystyrene DendriMacs/HyperMacs and polybutadiene DendriMacs described above we are taking advantage of the possibilities offered by living anionic polymerisation to control not only the molecular weight and polydispersity but also the composition of the macromonomers. Polybutadiene HyperMacs required little or no effort to realise. Introducing the appropriate AB<sub>2</sub> chain-end functionalities onto a macromonomer of PMMA proved more of a challenge but has been achieved. The key to this work was to switch the way the functionalities were introduced and to do away with the 3-*tert*-butyldimethylsiloxy-1-propyllithium initiator containing a protected primary alcohol functionality. In its place a diphenylhexyl (derivative) lithium initiator was used to initiate the polymerisation of PMMA (Scheme 7) thereby introducing the two phenol functionalities at the  $\alpha$  chain end. Excess 1,3-dibromopropane was used to introduce an alkyl bromide functionality at the  $\omega$  chain end through a controlled termination reaction. The resulting AB<sub>2</sub> PMMA macromonomers – with a variety of molecular weights – have subsequently been converted into PMMA HyperMacs.

### 6.1 HyperBlocks

Another exciting extension of the macromonomer approach is to produce macromonomers which are block copolymers. Anionic polymerisation gives us the opportunity to prepare macromonomers which are diblocks, triblocks and multiblock copolymers with a very high degree of control over molecular weight and copolymer composition. It is to be assumed that such highly branched block copolymers will still undergo microphase separation but it is a certainty

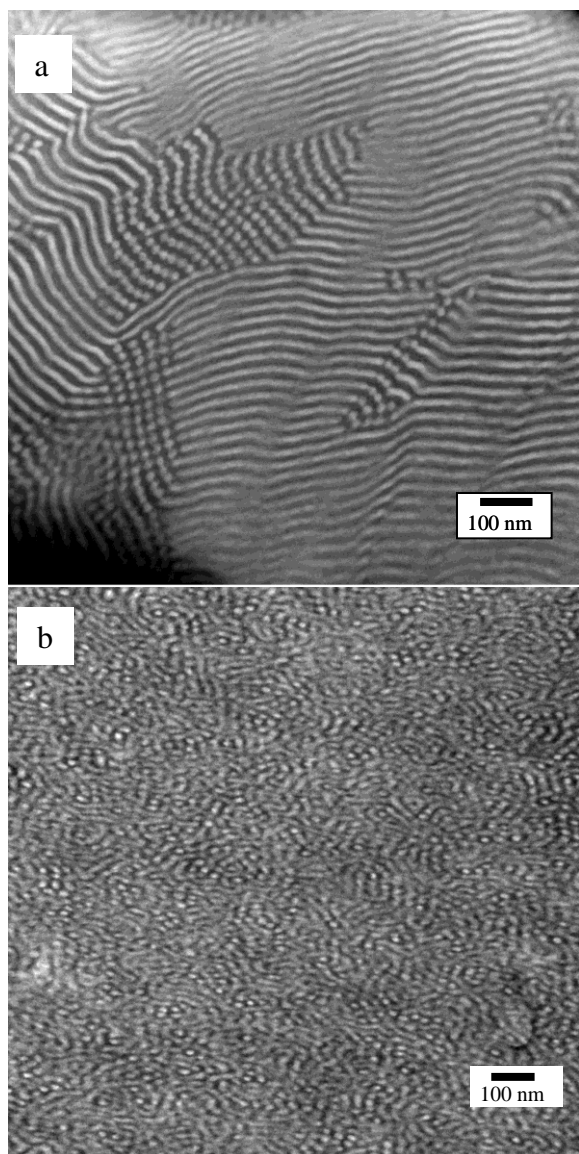


Figure 3. Transmission Electron Micrographs of a) linear PS-PI-PS triblock copolymer (macromonomer) and b) PS-PI-PS triblock copolymer HyperBlock

that, whether the copolymers be DendriMacs or HyperMacs, the highly branched architecture will frustrate phase separation leading to novel morphologies, smaller domains and less long range order. As a first attempt to explore these assumptions we have prepared macromonomers which are ABA triblock copolymers of polystyrene–polyisoprene–polystyrene (PS-PI-PS). HyperMacs prepared from these block copolymers (we have coined the term HyperBlocks to describe such materials) have been successfully prepared and both differential scanning calorimetry and dynamic mechanical analysis suggest microphase separated structures with two distinct glass transition temperatures. A programme to characterise the physical and mechanical properties of the HyperBlocks by TEM, x-ray scattering and mechanical testing is ongoing, however preliminary TEM

studies to establish the morphology of these copolymers appear to support our assertion that the highly branched structure frustrates phase separation and impacts on long range order. The TEM of a PS-PI-PS linear macromonomer (Figure 3a) shows a well-defined cyclindrical morphology with cylinders of polystyrene in a matrix of polyisoprene. The TEM of a HyperBlock (Figure 3b) made from this macromonomer also shows phase separation but with little or no long range order. Similar observations have been made for other highly branched ‘barbed wire’ copolymers. We hope and believe that these HyperBlocks may show promise as thermoplastic elastomers. Full details of these more recent studies will be described in forthcoming publications.

In summary; we have in recent years developed and described a methodology for synthesising two classes of long chain branched polymers – DendriMacs and HyperMacs. Although similar structures have been prepared by other methodologies we believe that the macromonomer approach, whereby well-defined linear polymers are prepared by living anionic polymerisation and are subsequently reacted in a coupling reaction to yield highly branched polymers, will emerge as one of, if not the most successful and versatile strategies.

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